On the Viscosity of Sulphur.

By C. Coleridge Farr, D.Sc., F.P.S.L., Professor of Physics, and D. B. Macleod, M.A., B.Sc., Lecturer in Physics at Canterbury College, University of New Zealand.

Historical.

A great amount of work has been done on the composition and properties of liquid sulphur by Prof. Alexander Smith and his collaborators, mainly at the University of Chicago.

The general conclusions arrived at by them may be briefly stated as follows : Ordinary liquid S consists of two modifications of sulphur known as S_λ and S_μ, of which S_λ is very soluble in CS_2, whereas S_μ is practically insoluble. The percentage composition of S_λ and S_μ in liquid S varies with the temperature, but provided the temperature has been kept constant for a sufficient length of time the percentage composition at any particular temperature is always the same, though various impurities such as SO_2, NH_3, H_2SO_4 may retard or accelerate the attainment of a state of equilibrium. The percentages of S_μ, when equilibrium has been attained, have been given by Smith and Holmes[*] and Carson[†] on a continuous curve from 120° C. to 440° C., and from this curve it seems that the S_μ varies from 3·75 per cent. at 120° C. to 34 per cent. at 440° C. A sharp rise in the percentage of S_μ takes place at about 160° C., corresponding with the increased viscosity of S about that temperature. An apparent exception to the general rule for impurities was found for iodine with which higher percentages of S_μ were obtained. Smith and his collaborators do not claim that the percentages given by them are the actual percentages in liquid S, as in the process of chilling some S_μ may revert to S_λ, and thus the percentage of S_μ may be too low. By chilling a stream of burning S they found a percentage of 51 per cent., which would seem to indicate that the value 34 per cent. at the boiling point as found by ordinary chilling was too low.

In this work on sulphur, though the viscosity is referred to, no exact measurements have been made, and only the temperature at which obvious thickening has taken place is referred to.

Not a very great amount of work has been done on the viscosity, though it has long been known to be anomalous. A résumé of work done prior

[*] Smith and Holmes, 'Z. Physik. Chem.,' vol. 54, p. 257 (1905).
[†] Carson, 'J. Amer. Chem. Soc.,' vol. 29, p. 499 (1909).

to 1905 is given by Rotinjanz in his paper on the changes in the viscosity of liquid sulphur,[*] but no results which are certain in their value have been obtained. Rotinjanz tested the viscosity by a modification of Ostwald's viscosimeter, and examined it from the melting point to the boiling point. All his experiments, however, seem to have been carried out with rather rapidly rising or falling temperatures, so that a state of equilibrium in the S, or even a state of uniform temperature could not be secured. His temperatures rose at rates varying from 0·27° C. to 2° C. per minute. His main results were that with moderate rates of heating (0·27° to 1° a minute) the sulphur reached a maximum of viscosity (52,000 relative to water) at 187° C., while with greater rates of rise of temperature the maximum of viscosity occurred at higher temperatures. On cooling S from temperatures above 230° C. the maximum viscosity was lower and the temperature at which it took place higher than with rising temperatures. He also found that the higher the temperature to which the S had been heated before the gradual cooling began the lower was the value of the maximum viscosity on the downward grade, and the higher the temperature at which it occurred.

Rotinjanz also states that S, through which NH_3 has been passed, has a maximum viscosity relative to water of 19,000 at 180° C., and he draws the conclusion that there is no connection between the viscosity and the percentage of S_μ.

We have been unable to find any later work on the viscosity of sulphur.

Method of Experiment.

On account of the great viscosity of S from 170° C. to 220° C., we found Ostwald's viscosimeter method unsuitable for determinations at these temperatures, though well suited to temperatures up to 160° C. We decided, therefore, to adopt the method of rotating cylinders for our determinations. Our method was as follows: A glass tube, D (fig. 1), sealed at one end, contained a thermometer, C, reading to 360° C., and sufficient mercury to give stability to the system, and also to enable the thermometer to take up its proper temperature quickly. This tube had an external diameter of about 1·4 cm., and the system weighed about 150 grm. This was suspended by a bifilar system, BB, passing over a small light pulley, A, and through two fine holes, FF, GG, is a small piece of iron, in which are fine holes at different distances from the central one, and the suspension wires passing through two of these would immediately be at a known distance apart at the bottom. This small plate of iron was slipped into a cap fitted on to the tube D. The small pulley, A, enabled the system to take up a vertical

[*] 'Zeit. Physikal. Chem.,' vol. 62, pp. 609–621 (1908).

position without further adjustment, and also secured the equal tension on each thread of the suspension. When measuring viscosity in sulphur, the length of the suspension was about 16 cm. and the width about 6·5 cm. Fine copper wire (0·019 cm. diameter) was used for the suspension. The tube D was lowered into a larger outer test-tube, E, of good cylindrical form, the internal diameter of which varied in the different measurements

Fig.1.
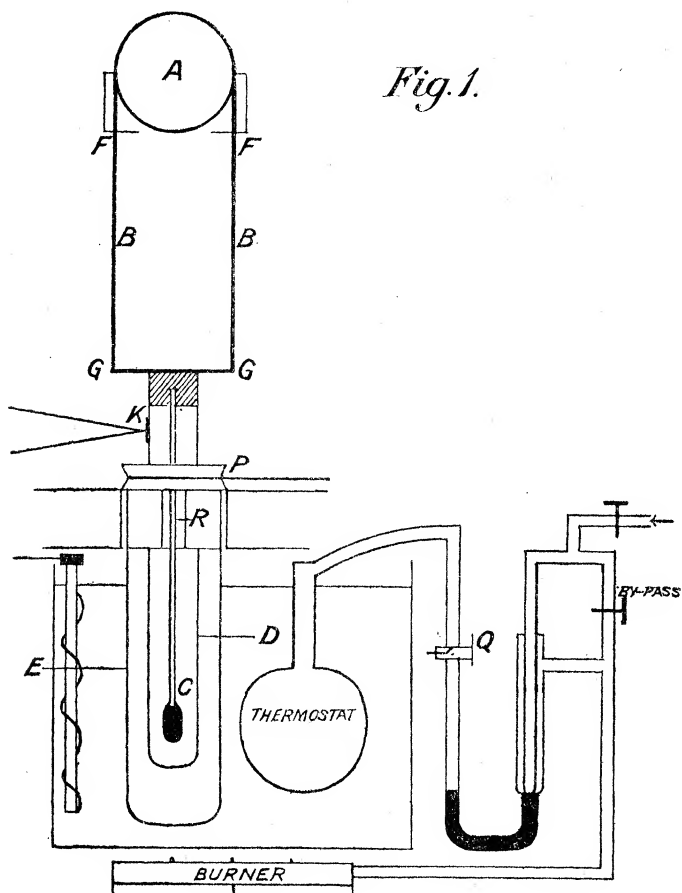
from 3 cm. to 3·5 cm. This test-tube contained the sulphur to be examined, and could be rotated by means of a pulley, P, at any desired speed. The pulley and system, into which the test-tube was packed with asbestos, rotated on a fixed stand, L, care being taken that the test-tube was vertical after being packed. A mirror, K, was attached to the tube, D, and the deflection was measured by the movement of the spot of light reflected from this mirror from a lamp on to a circular scale. In all later experiments a

paraffin bath was used, to give a temperature up to 220° C., the paraffin being vigorously stirred and the temperature governed by an air regulator. By means of a three-way tap at Q, any temperature desired could be quickly reached, and then maintained constant. By means of a window, R, in the framework holding the tube, E, the temperature of the thermometer, C, could be read and compared with the temperature of the bath. This was most important, as it was found that, on account of the poor conductivity of sulphur, it took as long as three-quarters of an hour for the two temperatures to become the same.

By altering the length of the suspension and the distance apart of the wires, any degree of sensitiveness could be obtained. For sulphur below a temperature of 160° C., a unifilar suspension was used, consisting of copper wire (0·019 cm. diameter), of length about 60 cm. With this arrangement the system was very sensitive (though, of course, it could have been made much more so), and had to be protected from air currents by a glass covering. The bifilar system was very stable, and took up its final deflection rapidly, and without much movement of the spot.

The expressions used to calculate the viscosity were the usual ones used for bifilar and unifilar suspensions, and for the rotating cylinder method, viz., for the bifilar

$$\eta = \frac{(a-b)(a+b)\,mgd_1d_2}{16\pi\,a^2b^2\,\omega hl}\,.\,\sin\theta,$$

where
$b =$ radius of inner cylinder.
a radius of outer cylinder.
m mass of suspended system in grammes (less amount due to displacement of S).
d_1 and d_2 width of suspension at top and bottom.
ω angular velocity of rotation of E.
h depth of immersion of tube D in sulphur.
l length of suspension.
θ angle of deflection.

The speed of rotation was taken with a stop-watch, and was generally of the order of one revolution in about five seconds. By means of lamp resistances and a motor with a magnetic brake the speed could be easily varied, and as a check the deflections at three or four different speeds were always taken.

For the unifilar suspension the expression used was

$$\eta = \frac{\pi l_1 m_1 (a_1{}^2 + b_1{}^2)(a-b)(a+b)}{12\,l\,T^2 a^2 b^2 \omega h}\,.\,\theta,$$

where T is the time of oscillation of a rectangular bar of mass m_1, about an axis perpendicular to its dimensions (sides), a_1 and b_1, and suspended by a wire of length l_1, which is the same wire as was used in the experiment.

These expressions were tested with glycerine and water, and gave good agreement with their known values. With reasonable care all the quantities could be measured within 1 per cent. of error.

We have found, like most other workers with sulphur, great difficulty in securing consistency in our results. An important part of this paper will be a discussion of these inconsistencies. On account of the enormous variations in the values of the viscosity of S at different temperatures, and also, as we shall show, with different samples at the same temperature, the viscosity of sulphur provides a far more sensitive method of noting changes in S than any other of its physical properties, such as density, coefficient of expansion, or surface tension.

In our early experiments the viscosity was studied with ascending and descending temperatures. By means of a mercury bath, temperatures up to 300° C. were obtained, though most of our work was done below 230° C., the highest temperature to which a paraffin bath could be taken with safety. Fig. 2 gives the general results obtained by this method. Curve I represents the viscosity curve of a sample of twice distilled S which had been collected in the ordinary way and allowed to crystallise. Curve I was taken with ascending temperatures, and the highest temperature reached was about 278° C. After reaching this temperature, the temperature was gradually decreased and readings taken (after seeing that the thermometer in the bath and that in the tube D read the same) at the same temperatures on the down grade as they had been on the up grade. In addition to these, special readings were taken at the maximum on both the up and down grades. The values of the viscosity with falling temperatures are shown in curve II as they are with rising temperatures in curve I. Curves III and IV give the values after allowing the sulphur to remain heated to 150° C. during the night, curve III with ascending temperatures, and curve IV with descending. The values of the viscosity in these curves are given in arbitrary units only, though all later values are given in C.G.S. units. Two things are to be noticed from these curves: (a) the marked lowering of the viscosity with descending temperatures, thus confirming the results of Rotinjanz (loc. cit.) (As was also pointed out by him, the lower the maximum value of the viscosity the higher the temperature at which it occurs), and (b) the marked effect of keeping the S at a temperature of 150° C. for 18 hours.

A series of experiments was next made with a view to connecting, if possible, the amount of S_μ present in the S with the viscosity. Test-tubes

containing some of the same sample of S as was being used for the viscosity test (as a general rule twice distilled S) were placed in the bath along with the viscosity tube, and as the tests for viscosity were made at various temperatures a small test-tube was withdrawn and plunged into ice. This small test-tube had a smaller rod of glass within it, in order to confine the

Fig. 2.
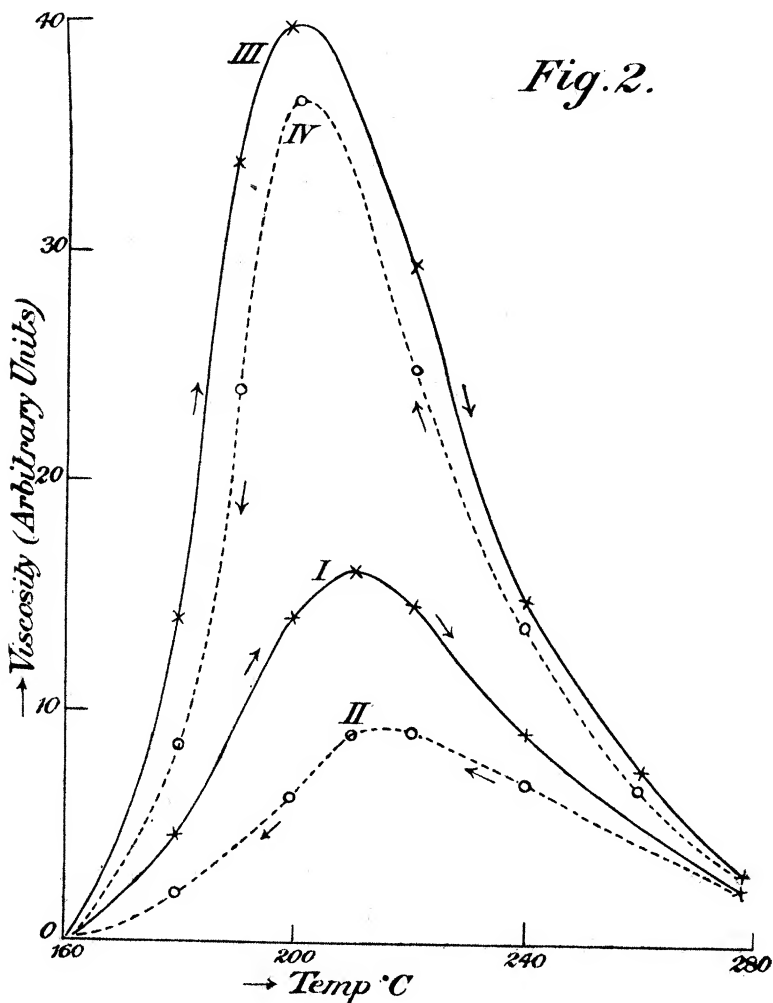
S to be analysed for S_μ to a film on the outside, so that it might all quickly cool. The analysis was done in the same way as by Smith and Holmes.* The temperature was kept constant till the thermometer in the bath and that in the tube D read the same.

* 'J. Amer. Chem. Soc.,' vol. 27, No. 8 (1905).

The results from this set of experiments are illustrated in fig. 3, the individual experiments being marked 1, 2, 3, and 4.

Fig.3.
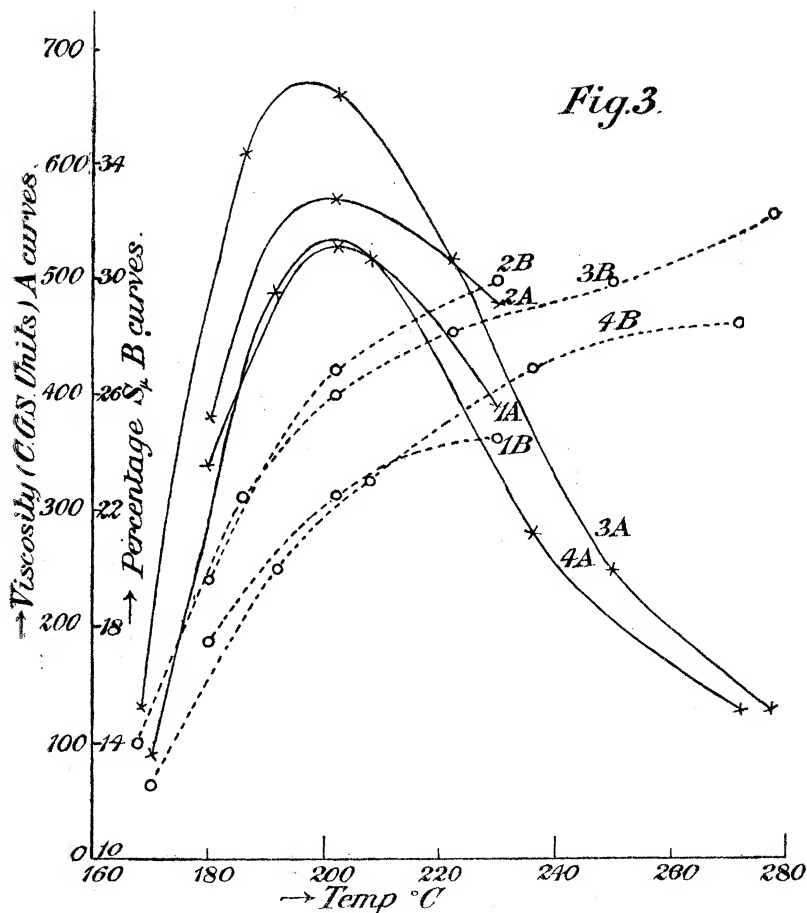
The experiments illustrated in the curves marked 1 and 2 were taken with the same sample of sulphur, but curve 2 after a greater period of heating. Curves 3 and 4 refer to samples different from 1 and 2 and from each other. The corresponding curves for viscosity and S_μ are marked A and B respectively. Thus 2 A is the viscosity curve corresponding to the S_μ curve 2 B. These curves indicate that different samples have different percentages of S_μ, and also that the higher the percentage of S_μ present the greater the viscosity at any particular temperature. In this respect curve 2 is not in such good agreement with curve 3 as the other samples.

A series of measurements, using the unifilar suspension, was next made at temperatures below 160° C. Consistent results were obtained at these

temperatures, though we have not examined the viscosity under such varied conditions as at higher temperatures. A sample of twice-distilled sulphur was maintained at a temperature of 135° C. during the night and tested the following day. The deflection given is a mean of eight or ten different readings at each of several different speeds, as the unifilar deflection was not so steady as the bifilar. The values of the deflection at the different speeds of rotation were reduced to the same speed, and the agreement between the observations was then very good. Other samples of twice-distilled sulphur gave similar values.

| Temperature.	Viscosity in C.G.S. units.	Deflection in mm.
° C.		
123 ·0	0 ·1094	111
135 ·5	0 ·0866	88
149 ·5	0·0709	72
156 ·3	0 ·0719	73
158 ·2	0 ·0759	77

These figures indicate a minimum viscosity in the vicinity of 150° C. An undoubted increase had taken place at 158·2° C. On raising the temperature to 160·5° C. the deflection became too great for the system, indicating a decided increase between 158·2° C. and 160·5° C. As far as we have at present investigated it, the change in viscosity in the neighbourhood of 160° C. is not of the nature of a sharp and abrupt change, but a gradual bending round, and can be traced back at least as far as 158° C. Though we have not yet made a special series of experiments at 160° C., the following were observed at temperatures from 159·2° to 160·3° C. :—

Temperature.	Viscosity.	Temperature.	Viscosity.
° C.			
159 ·2	0 ·0948	160 ·0	0 ·2283
159 ·5	0 ·1445	160 ·3	0 ·7732

A later experiment, in which the minimum was especially sought, confirmed the statement that a definite increase had taken place at 158·2° C. above that at 152° C., and also that the change from 158·2 C. to 160° C. was gradual, and that over this small range of temperature the change is elastic (it is not so over great ranges of temperature), and that lowering the temperature reproduced the results obtained on the upward grade. To show the character of the changes observed, the following deflections, which were the mean in each case of 40 oscillations, may be quoted :—

Temperature.	Deflection.	Temperature.	Deflection.
° C.		° C.	
140·0	116·5	158·5	112·8
152·0	100·0	159·4	212·0
158·3	108·8		

Fig. 4 gives a graphical representation of the changes to 163° C. We consider that the evidence of the viscosity is that there is not a transition point in the


Fig. 4
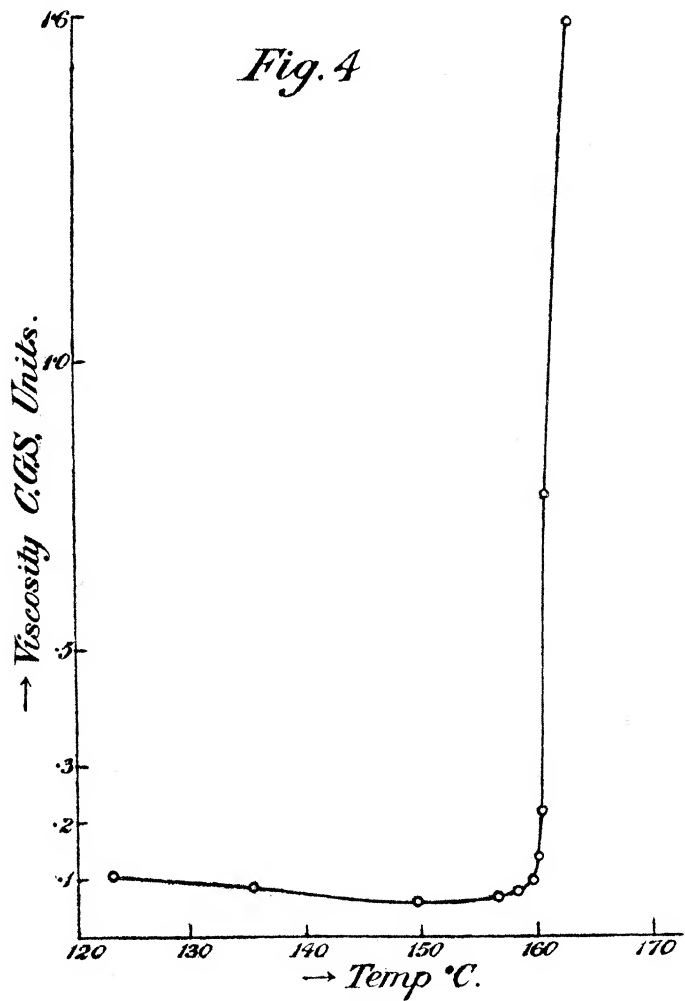
strict sense of the word in the neighbourhood of 160° C., though the viscosity undergoes a marked increase in the range of a few degrees from 159° C. to 163° C.

It is in the range of temperature from 160° C. to 230° C. that we have found the most marked variations in the values of the viscosity of different samples of sulphur of seemingly equal purity, when the viscosities of those samples were compared at the same temperature within this range, and it is here consequently that most of our work has been so far done. In view of the work of Smith and his collaborators, and their opinion that sulphur through which NH_3 had been passed takes up an equilibrium value between S_λ and S_μ ($S_\lambda \leftrightarrows S_\mu$) rapidly, we had hoped to obtain a consistent sample by ammoniating twice-distilled sulphur. It was very soon noticed, however, that the amount of NH_3 absorbed had a great effect upon the viscosity of the S. Sulphur has the power of absorbing great quantities of gas especially NH_3 and SO_2, and on passing either of these gases through molten S at 150° C. for several minutes and then allowing the sulphur to crystallise, large quantities of gas were given off, so much so that a large blob was formed at the surface of the sulphur at the time of crystallisation due to the gas forced out of solution by this act. Notwithstanding this, further considerable quantities are evolved on remelting. We have found as the result of many repeated experiments that sulphur through which NH_3 has been passed for several minutes gave over the range 160° C. to 180° C. a fairly "low" valued viscosity curve, but on allowing the sulphur to crystallise, and consequently rid itself of considerable quantities of dissolved gas, the viscosity value at any temperature invariably rose, giving what we term a "high" curve. It was observed that S saturated with ammonia at 150° C. tended to give off the gas between 170° C. and 180° C., but on account of the great viscosity, the gas was not able to escape from the mass. The experiments illustrated by fig. 5 show that irrespective of the value of the viscosity of the S used, samples saturated with NH_3 give consistent values, and also samples from which a certain amount of the gas has been driven out by crystallisation. On remelting, intermediate values are obtained when the sulphur had been crystallised but not allowed to cool.

In fig. 5 the viscosities at different temperatures of the original four samples of twice-distilled S are marked with a circle. On saturation with ammonia at 150° C. and then determining the viscosities at different temperatures the different values obtained are marked with a triangle. On crystallising but not allowing to cool below about 119° C. (the melting point), then rewarming and redetermining viscosities, the values obtained are marked with a cross enclosed in a circle. Finally crystallisation, cooling to ordinary temperatures by allowing the sulphur to remain all night in the crystalline form, and then reheating and determining viscosities again next day, gave the different values marked with the cross. It will be seen that a quite satisfactory curve will

pass (*a*) through the triangles, and (*b*) through the crosses, whilst the values obtained from the other two methods of procedure are irregularly distributed

Fig. 5.
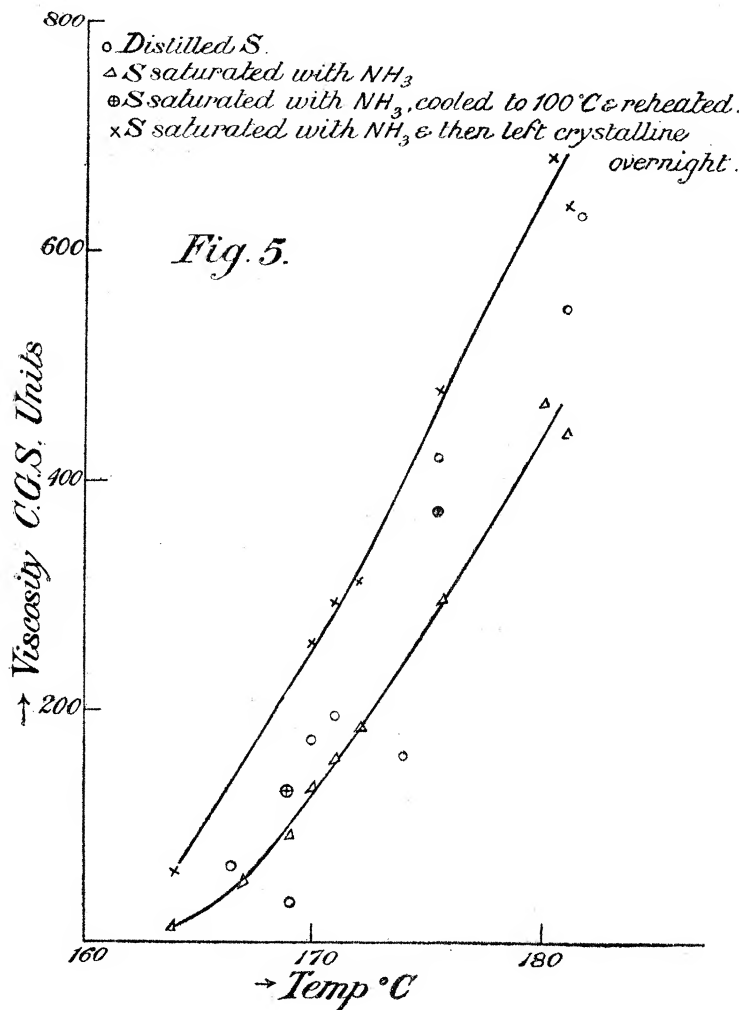
about. Smith and Holmes (*loc. cit.*) argue from the behaviour of ammoniated S that the percentage of S_μ in ammoniated sulphur is the same as in ordinary sulphur, but the experiments do not support the view that the viscosity is a function of the amount of S_μ present. It is possible that large quantities of dissolved gas may reduce the viscosity by simple mechanical means.

A similar experiment with SO_2 instead of ammonia gave a lower value with excess of SO_2 than when it had been allowed to crystallise out.

These results show that the viscosity of sulphur treated with either NH_3 or SO_2 depends largely on the amount of these gases present. We are,

however, leaving the whole question of the effect of dissolved gases for a later paper.

Temperature.	Viscosity.	Remarks.
° C.		
171 ·0	181 ·5	Twice-distilled sulphur.
171 ·0	161 ·0	Sulphur saturated with SO_2 at 150° C. and then reheated.
171 ·0	185 ·0	Sulphur allowed to crystallise and then reheated.

With ordinary twice-distilled sulphur the results were irregular. It was, however, found that if the sulphur were distilled and somewhat rapidly cooled, so that it became solid soon after flowing into the receiving flask, and so that there was no great quantity in the liquid form in the receiving flask, a low viscosity curve was obtained. On the other hand if the sulphur was distilled so rapidly that it remained liquid in the receiving flask until the operation of distillation was completed, a somewhat high valued viscosity curve resulted. Moreover, on keeping a low or medium valued sulphur at any temperature from 120° C. to 160° C. for a length of time, the viscosity, as measured at some temperature between 160° C. and 190° C. (the viscosity was generally measured at about 171° C.), invariably rose, finally reaching a maximum. This change was a slow one, in some cases as much as 36 hours elapsed before the viscosity reached its final value, and it always required some 18 or 20 hours. Also repeated crystallisations had the effect of slowly raising the viscosity of a low sample. As has been found also by Rotinjanz, if a sample of comparatively high valued viscosity were heated to 230° C. or higher and then recooled to 170° C. its viscosity was diminished.

In illustration of these results the following experiments may be quoted: In these experiments the viscosity was tested at 171° C., though occasionally the temperature was raised to 180° C., and again lowered at 171° without appreciable change in the viscosity. The effect of crystallisation is shown by the following typical experiment :—

Temperature at which the viscosity was measured.	Viscosity.	Remarks.
° C.		
171 ·0	100	Twice-distilled sulphur.
171 ·0	121	The sulphur was then allowed to remain crystalline all night.
171 ·0	141	Crystallised through night as before.
171 ·0	164	Crystalline over week end.
171 ·0	176	Crystalline over night.

No gradual increase (proportional to time) nor other effect was observed owing to the sulphur remaining long in the solid state, as two samples, one giving a low value and the other a high, were left in their tubes for four weeks, but, on retesting, gave similar values to their previous ones, the lower one only having risen by the amount due to a single crystallisation, and the higher one remaining constant.

The following experiment shows the combined effect of crystallisation and of keeping the sulphur for stated lengths of time at a temperature of 125° C. The temperature at which the viscosity was measured was 171° C. throughout :—

| Viscosity.	Remarks.	Viscosity.	Remarks.
57 ·2	Twice-distilled S, quickly cooled.	284 ·6	3 hours at 125° C.
90 ·4	Kept 3 hours at 125° C.	284 ·6	Crystallised through night.
102 ·4	Crystallised throughout night.	336 ·3	3 hours at 125° C.
133 ·0	3 hours at 125° C.	336 ·5	Crystallised through night.
143 ·3	Crystallised during night.	368 ·5	4 hours at 125° C.
187 ·5	4 hours at 125° C.	347 ·0	Crystallised through night.
196 ·8	Crystallised through night.	375 ·1	4 hours at 125° C.
242 ·0	4 hours at 125° C.	425 ·7	All night at 125° C.
247 ·3	Crystallised during night.		

It will be noticed that, while the sample has a low viscosity, crystallisation seems to raise it. This may possibly be partly or wholly due to the fact that in order to crystallise, the sulphur has to cool down somewhat slowly from 171° C. (the testing temperature) to the solidifying point, and then next day has been rewarmed through the same range of temperature, during which there would be an increase in accordance with the proved effect of keeping it in the limpid condition. But while this may be so, it is difficult similarly to explain the slight lowering effect which crystallisation certainly seems to have on a high valued sample.

A similar experiment in which the temperature was 141° C. instead of 125° C. gave similar results, though the viscosity rose more rapidly. After 22 hours' heating in three and four-hour periods the viscosity rose from 80·7 at 171° C. to 393 at the same temperature, and after then remaining all night at 141° C., it rose still further to 466 at the same testing temperature. Two consecutive crystallisations reduced this to 440, but on again heating it all night at 141° C. it rose to 470 (tested at 171° C.) which, therefore, seems to be a maximum for that temperature. A similar maximum had been obtained on another occasion after prolonged heating.

On then passing ammonia into this high valued sample (470) its viscosity fell to 282 (as measured at 171° C.), but rose again to 326 on allowing the sulphur to just crystallise and then reheating to the testing temperature, thus confirming in a general way the previous values with NH_3.

With a view to tracing the cause of these changes a series of experiments was made in which the sulphur was heated in a vacuum and under nitrogen. Three experiments were made in which the sulphur was placed in a vessel consisting of two distilling flasks fused together as in fig. 6. The sulphur was drawn into the flasks in a molten condition, and the lower leading tube

Fig. 6.
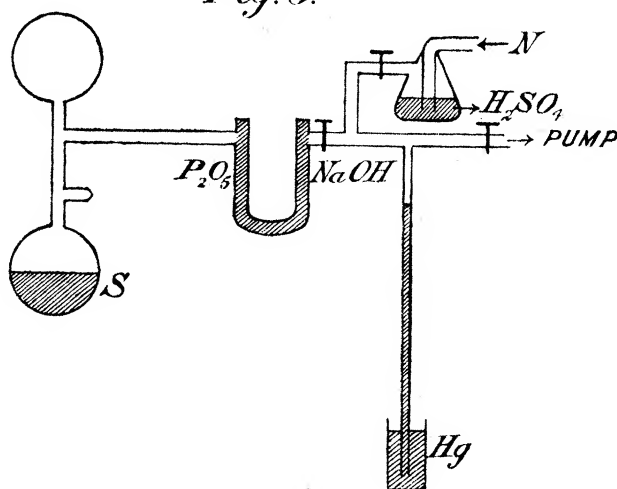
was then sealed off. The other was connected to a motor-driven oil vacuum pump capable of exhausting down to about 3 mm. or less, and also through drying tubes of P_2O_5, NaOH, and H_2SO_4 to a reservoir containing carefully prepared nitrogen. The sulphur in the lower flask was then melted under a vacuum and kept for some time at a low temperature under this vacuum, until at any rate all the visible bubbles of dissolved gas had been pumped out. The temperature was then allowed to rise, and as it rose N was admitted until the sulphur finally boiled under N at atmospheric pressure. The temperature was several times lowered to allow the flask to be evacuated again, and N was then reintroduced and the boiling repeated. The flasks were finally sealed off and one-half of the sulphur was decanted *in vacuo* into the upper flask, and there allowed to crystallise. The sulphur at the other end was kept at a temperature of about 140° C., or 150° C. for several days in an electric oven, out of which the crystallised half protruded and was thus kept cool. The viscosity of the two samples was then tested at

171° C. The viscosities in C.G.S. units in the case of two such sets of experiments A and B were as follows :—

	Portion kept crystalline.	Portion kept liquid at 150° C.	Remarks.
Experiment A ...	128	65	Kept at 150° C. for 24 hours.
Experiment B ...	251	182	Kept at 150° C. for 4 days.

The samples used in Experiment B were then exposed for 24 hours at a temperature of 150° C. to air, and then again tested for viscosity at 171° C., with the result that the viscosity of the portion which had been previously kept crystalline rose to 489, whilst that of the other was 484, and that of a third portion, kept for 24 hours in a semi-viscous state, at a higher temperature than 150° C., only rose to 396.

In a third experiment with the two flasks, the upper flask (the empty one) was thoroughly heated before decanting, with a view to driving off any impurity, such as H_2SO_4, that might have condensed there before decanting half the sulphur from the other end into it. In this case, the viscosity of the crystalline portion gave, at 171° C., a lower value (131) than that of the liquid portion.

On a drop of H_2SO_4 being added to the portion which had been kept liquid, without any special effort being made to produce complete diffusion, the viscosity (always tested at 171° C.) rose immediately to 222 C.G.S. units.

To test this question further, the previously crystalline portion (viscosity 131) was transferred to a smaller distilling flask, and again heated under a vacuum, and boiled under nitrogen, special care being taken to heat most thoroughly the upper part of the flask during the evacuations, in order to drive off any H_2SO_4 which might possibly have condensed there. By this process, the viscosity was reduced from 131 C.G.S. to 78 C.G.S., both measured at 171° C.

These experiments show that, whereas keeping sulphur exposed at a temperature of 150° C. to air, resulted in a rise of viscosity, in one instance from 182 C.G.S. to 484 C.G.S. in 24 hours, keeping it at 150° C. under a vacuum for five days resulted in the viscosity being actually lower than that of the sample of the identically same sulphur kept crystalline.

The results were still unsatisfactory, however, in that they failed again to give consistent results for the final values, presumably because they failed to remove the impurities present in the sulphur, such impurities as H_2SO_4 being able to condense in the cool upper flask.

With a view to preparing a sample of special purity without, however,

going to the extreme precautions used by Threlfall and Brearley* (as we were rather seeking the effect of dissolved gases and their products than of such solid impurities as selenium and arsenic), commercial rolls of sulphur were first filtered hot, and then carefully distilled four times in very specially cleaned retorts and receivers, the first and last portion of each distillate being rejected. During the last distillation, the sulphur was rapidly cooled by allowing it to flow into a receiver kept floating in water, so that there was never more than a few cubic centimetres of it liquid in the receiver at any time. The final product presented a uniform colour, and had the appearance of purity, and in neither of the last two distillations were there any of the "black spots," which are so frequently mentioned by workers with sulphur, left in the retorts. We may say that we consider these black spots are "ordinary dirt" of almost any kind, which sulphur is very prone to take up and conceal. We think there can be no doubt that liquid sulphur is a very great solvent both of gases and solids. Two portions of this sulphur, which had been boiled under nitrogen for about an hour and sealed off under a vacuum, gave for viscosity at 171° C. the values 95 C.G.S. and 120 C.G.S. respectively. The second sample had been kept at 200° C. for about three hours and at 150° C. for 24 hours (both under a vacuum), but the difference of viscosity was probably due to the less vigorous boiling and heating of the upper portion of the flask. A third portion of the same sulphur was therefore taken, and submitted to a more vigorous boiling, heating, and evacuating. Before melting the sulphur in the small flask in which it was contained, the flask and solid sulphur in it were evacuated to a few millimetres of mercury twice, and each time purified nitrogen was admitted. It was then re-evacuated, and the sulphur was melted under a vacuum. As usual, a large volume of gas escaped. When no further gas appeared, the temperature was raised, and nitrogen allowed to pass in slowly, until the sulphur boiled at atmospheric pressure under nitrogen. The sulphur was kept boiling for $5\frac{1}{2}$ hours, and the vessel in which it was contained was evacuated four times during the process. It was necessary for this purpose to allow the sulphur to cool to about 300° C. The upper part of the neck of the flask was frequently and vigorously heated, and the flask was finally pumped out to a few millimetres of mercury and sealed off. The sulphur, on being allowed to crystallise, presented a uniform appearance, but of a quite unusual character, the crystals being needle-like and of a transparent greenish colour, totally different from the original colour of the sulphur. This greenish appearance had been noticed before with sulphur which had been boiled for some time and allowed to crystallise *in vacuo*, and

* 'Phil. Trans. R. S.,' A, vol. 187 (1896).

was at first thought to be due to an impurity, but, when later the flask was broken open, and a small portion of the melted sulphur recrystallised whilst exposed to air, it quite regained its original yellow appearance, showing that the greenish colour is due to the sulphur being gas-free. It is possible that these greenish crystals may approach pure monoclinic sulphur.*

It happened that this purified evacuated sulphur was kept for 48 hours *in vacuo* before the flask was opened and the viscosity tested. During that period very small patches of the yellow opaque sulphur had begun to develop, but the change seemed slower than usual, and it is possible that, with still greater purity and a better vacuum, the greenish variety might not revert to the yellow. For the viscosity test the sulphur was remelted *in vacuo*, and quickly transferred to the testing tube in the bath, which had been adjusted to 171° C., and the test was made as soon as the thermometer within the inner tube had reached 171° C. Readings of the viscosity were also taken at the other temperatures given below. No diminution in the viscosity on the downward grade of temperature was observed after the temperature had risen to 220° C. and was being cooled again. We consider that these values of the viscosity are a near approach to the values for pure gas-free sulphur :—

Temperature.	Viscosity in C.G.S. units.	Temperature.	Viscosity in C.G.S. units.
° C.		° C.	
165·0	5·0	200·0	215·0
171·0	45·0	210·0	205·0
184·0	160·0	217·0	191·0
190·5	197·0	220·0	186·0
197·5	213·0		

This last experiment, together with the previous ones, shows conclusively that the presence of air is necessary for the production of a sample of sulphur with a very high viscosity curve, and, as some form of oxidation is undoubtedly the effect of exposure to air, SO_2 or H_2SO_4 are the substances most likely to be producing the effects.

SO_2 does not appear to be the chief disturbing impurity, because—

(1) Repeated crystallisation and remelting under a vacuum which would remove dissolved gases should show a marked effect on the viscosity, whereas these alone have proved to be incapable of reducing the viscosity of a high sample.

* Though, as has been pointed out to us by Prof. Evans, experiments are needed to show that this greenish colour is not due to impurities derived from the glass, the colour of which alters on slight oxidation.

(2) Freshly distilled sulphur which invariably contains SO_2 gives both low and high values, the result depending apparently on the rapidity of cooling.

(3) Passing SO_2 into sulphur even to saturation has only a comparatively slight effect on the viscosity.

In favour of H_2SO_4 the following considerations may be adduced:—

(1) The impurity received on exposure is not removed below a temperature of about 220° C., about the temperature at which H_2SO_4 finally dissociates. The lower values of the viscosity on the descending temperature, observed by Rotinjanz and ourselves after a temperature of 220° C. has been reached, can be explained by the dissociation of the H_2SO_4 present in the S.

(2) The great difficulty in removing the impurity even with continued boiling suggests H_2SO_4, which would readily recondense in any cool portion of the flask.

(3) The low valued viscosity sample of sulphur which results from a rapid cooling to the solidification temperature may be explained by the H_2SO_4 not having had an opportunity to form in any quantity.

(4) The generally high value which results from allowing the sulphur to distil so quickly that the stream of molten sulphur flowing into the receiving flask keeps that already there in a melted condition throughout the whole operation—that is to say, at about a temperature of 150° C.—is on this view due to the exposure in thin extended layers of sulphur at a temperature of 150° C. to the oxidising effect of the atmosphere. Keeping a low or medium valued sample at a temperature within the very viscous range (160° C. to say 200° C.) does not in the same way increase the viscosity on account of the immobility of the particles.

(5) On distilling sulphur, or on boiling it in distilling flasks, small drops of a clear liquid, which could not have been water on account of the temperature, were frequently noticed in the cooler portion of the flask.

(6) Other workers[*] have shown that H_2SO_4 occurs in sulphur which has been exposed to air and have found it hard to remove.

(7) The effect of a drop of H_2SO_4 was to markedly increase the viscosity of a medium valued sample.

Thus, we incline to the view that sulphuric acid is largely responsible for the main increase of viscosity with exposure in a molten (but non-viscous) condition to the air, but while this is so we have shown that other impurities such as NH_3 and SO_2 have also an effect and that the effect seems to depend on the amount of impurity present. We differ, therefore, from Smith and his co-workers who consider that the effect of H_2SO_4, SO_2 and NH_3 is merely to retard or accelerate the attainment of a state of equilibrium which is finally

[*] Kellas, 'Jour. Chem. Soc.,' No. 674, p. 903 (1918).

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independent of the nature of the impurity present. Each sample of sulphur behaves as a distinct sample giving a distinct curve, and the temperature could be raised 20° or 30° and allowed to fall again without any change taking place in the viscosity as measured at a fixed temperature (usually 171° C.) each time, proving as it appears to us that it was not a case of equilibrium merely.

Summary of Results.

(1) The viscosity of purified (twice distilled but not gas free) sulphur has a value at 123° C. of 0·1094 C.G.S. units. It falls to a minimum of 0·0709 at 150° C. and then gradually rises to about 159° C. when the rise becomes more marked, but nothing of the nature of a strict transition point is observed.

(2) Exposure to air in a molten condition, especially below 160° C., has a most marked effect on the viscosity from 160° C. onwards. The effect is a slow one, the viscosity continuing to rise (as measured at 171° C.) for as much as 48 hours on exposure for that time to the air.

(3) The maximum for purified unexposed (gas-free) sulphur is reached at about 200° C. and has a value of 215 C.G.S. units; the maximum for purified (not gas-free) sulphur, but after prolonged exposure to the air is reached at a lower temperature, viz., about 190° C., and can have a value as high as 800 C.G.S. units.

(4) Crystallisation has an apparent effect (though it may be a secondary effect) upon the viscosity as measured at any temperature. It apparently raises the viscosity (as measured at any temperature, say 171° C.) of a low valued sample of sulphur and lowers the viscosity of a high valued sample. The effect of crystallisation seems to disappear when the viscosity of the sample (as measured at 171° C.) is about 300 C.G.S. units.

(5) H_2SO_4 appears to be the chief impurity (formed from exposure to the air) which causes the extreme variations which are to be found in the values of the viscosity of air-exposed sulphur. Dissolved gases such as NH_3 and SO_2 also affect the viscosity.

(6) Evidence is adduced that the variations in the viscosity are accompanied by a corresponding variation in the amount of insoluble sulphur present.

We are continuing these investigations.